

Moisture adsorption in optical coatings

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Summary

The thin-film filter is a very attractive large-aperture component which is exceedingly useful because of its small size, flexibility and ease of mounting. Thin-film components, however, do have defects of performance and especially of stability which can cause problems in systems particularly where long-term measurements are being made. Of all the problems, those associated with moisture adsorption are the most serious. Moisture adsorption occurs in the pore-shaped voids inherent in the columnar structure of the layers. Ion-assisted deposition is a promising technique for substantially reducing moisture adsorption effects in thin-film structures.

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1 Introduction

Of all the problems associated with thin film optical systems those associated in some way with moisture are the worst. The effects range from optical through mechanical to chemical and from obvious to subtle. Sometimes the effects may not be clearly and immediately attributable to water but in virtually any kind of thin-film instability, it is almost certain that eventually moisture will be found to be playing at least a supporting role if not the principal one.

In the 1960's, the industry as a whole was largely to have been unaware of the extent of the problem, although it is clear that some workers had identified water adsorption as an important agent in inducing instability. Koch made the connection between film microstructure and moisture penetration¹. Schildt et al² studied the influence of residual water vapor in the coating plant on the position of filter pass bands. Billings in a comment on the Schildt paper mentions his experience at Baird Atomic of uneven moisture ingress. Later, Barr³ describes a curious crystalline appearance that can be seen in narrowband filters, Meaburn⁴ writes of a curious phenomenon that he suspected was some kind of low temperature recrystallization, and Heitmann⁵ observes a curious flecked appearance of laser-mirror coatings that gradually disappears with time. With hindsight, all of these effects can almost certainly be attributed to moisture.

2 Film microstructure

To understand the effects of moisture we need first of all to understand the microstructure of evaporated thin films. Evaporated thin films follow the empirical Movchan-Demchishin⁶ model of film growth in which substrate temperature is the important determinant. Here the growth modes are divided into three zones, I, II and III, defined by substrate temperatures of less than $0.3T_m$, between $0.3T_m$ and $0.45T_m$, and above $0.45T_m$, respectively, where T_m is the melting point of the evaporant. Zone I is characterized by a loosely packed pronounced columnar microstructure with considerable void volume. Zone II is still columnar but has rather tighter packing. Zone III is a densely packed region in which the basic structural units are equiaxed crystallites rather similar to material solidified from the melt. Many thin-film materials, especially the refractory oxides, fall into Zone I because a sufficiently high substrate temperature for Zone II is not normally obtainable in a coating plant. Zone II growth is achieved by only a few materials. Thus the predominant microstructure in evaporated thin optical films is a columnar one.

The columnar structure brings with it a considerable void volume, the voids pore-shaped and running across the film, and a considerable internal surface area, much greater in total area than the simple external film surface. The departure from solidity of the film is described by the packing density, p , defined as:

$$p = \frac{\text{volume of the solid part of the film}}{\text{total film volume (i.e. solid plus voids)}}$$

Optical thin films usually have packing densities in the range 0.7 to unity and most often from 0.8 to 0.9. A packing density of 0.8 implies 20% void volume.

The microstructure has a profound effect on almost all properties of the films.

3 The effect of microstructure on film properties

3.1 Optical properties

The influence of microstructure on the optical properties of thin films has been a subject of some interest for at least one hundred years. The classical papers of Maxwell-Garnett^{7,8} were an attempt to calculate the optical properties of structured materials. The refractive index of a solid made up of two or more phases is very dependent on the extent to which surface charges screen the interior of the higher dielectric constant material. When the higher dielectric constant material is dispersed in such a way that there can be no continuous path for the electric field through it, then the screening charges will tend to push the electric field into the lower dielectric constant material with the result that the dielectric constant, and hence refractive index, is depressed. Maximum screening is associated with a series of parallel plates arranged normal to the direction of the electric field. Zero screening where the electric field readily enters the high-index material, is associated with plates parallel to the direction of the electric field. Since these are the two extremes then the refractive index of any structured solid will lie in between these two limits. If we represent the refractive index of the solid material of the film by n_s , that of the material in the voids by n_v and of the composite film by n , then for maximum screening,

$$n^2 = \frac{n_s^2 n_v^2}{p n_v^2 + (1-p) n_s^2} \quad (1)$$

while for minimum screening,

$$n^2 = p n_s^2 + (1-p) n_v^2 \quad (2)$$

The maximum and minimum screening structures are rather unlikely in thin film systems deposited in the normal way and illuminated at normal incidence. The limits to the refractive index in practice appear to be a simple linear interpolation⁹ of form:

$$n = p n_s + (1-p) n_v \quad (3)$$

and an expression associated with an array of cylindrical columns, a case included in an analysis by Bragg and Pippard¹⁰ with result:

$$n^2 = \frac{(1-p) n_v^4 + (1+p) n_s^2 n_v^2}{(1+p) n_v^2 + (1-p) n_s^2} \quad (4)$$

Cylindrical columns of identical radius will begin to touch and destroy the screening at a packing density around 0.9, and so we would not expect the Bragg and Pippard Law to apply above packing densities of around 0.9. Here the refractive index rises rapidly usually to the linear interpolation formula, (3). The behavior for packing densities below 0.9 depends on the details of the microstructure with the Bragg and Pippard expression applying to lower packing densities with well-defined columns and therefore well-developed screening. Voids shaped so as to permit the columns to touch at lower packing densities inhibit the screening effects to a greater or lesser extent, raising the refractive index above the Bragg and Pippard limit. This behavior has been studied by Harris¹¹ for dielectric films, using a finite element calculation and although little experimental data are available some comparisons can be made¹² with results achieved by Martin¹³ and Netterfield¹⁴ and the agreement is good. For oblique incidence, where the electric field is not normal to the columnar axis, the calculation of refractive index is more complicated. Measurements of such birefringence have been made^{15,16} and also lend support to the model. Variations in microstructure as the material grows leads to inhomogeneity¹⁷, a common feature of thin films especially the refractory oxides.

3.2 Mechanical properties

Thin films are almost invariably in a state of stress¹⁸. The stress in the films can be divided into an intrinsic and an extrinsic component. The intrinsic stress is that appearing inherently in the deposition of the material and existing at precisely the deposition temperature. The extrinsic component largely derives from the differential contraction that occurs on cooling from the deposition to the ambient temperature and is sometimes called thermal. The intrinsic stress is a consequence of the microstructure and the bonds that link across the gaps between the columns¹⁹. Packing densities of lower than 0.9 where the columns are not quite touching will, therefore, tend to have intrinsic tensile stress while those materials that form with packing densities higher than 0.9, where the columns are butting against each other, tend to compressive stress. The refractory oxides and the fluorides are examples of the former kind while zinc sulfide and selenide, materials with high packing density, exhibit compressive intrinsic stress²⁰. Because of the anisotropic nature of the films, the properties show considerable variation with direction in the films. The mechanical strength of the films is poor in any direction normal to the column axes. Since the intrinsic stress is biaxial in the plane of the film, and the film is weak in planes normal to this stress, tensile cracking is a frequent form of film failure. Tensile cracking is one form of strain energy dissipation. Thin-film adhesion failures are characterized by a progressive delamination known as a peel adhesion failure. In peel failures the work that must be done to propagate the failure balances the energy of the freshly created surfaces together with any energy dissipated in plastic deformation²¹. Strain energy is frequently sufficient to meet the surface energy needs and then all that is necessary for a failure to take place is a stress concentrator to create a force sufficient to break the bonds, usually some form of defect. The principal mechanism for compressive stress relief is delamination often accompanied by a buckling of the film that can result in beautiful zig zag patterns. Blistering in which a growing dome forms above the site of a failure, is a different form of compressive failure. Tensile strain energy can also result in delamination, usually exhibiting a curling up of the film edges, or it can be dissipated in the stress cracking referred to above which can occasionally dissipate sufficient energy to render delamination unlikely.

4 Moisture adsorption

4.1 Adsorption in single films

Films that are exposed to the atmosphere, adsorb atmospheric moisture. At low values of relative humidity the major effect of the adsorption is a relatively even coverage of the entire inner and outer surface of the film with a single monomolecular layer of moisture. Strictly the coverage is multilayer but the bonding between the moisture and fresh surface is very strong, usually chemical in nature^{22,23}, so that the second and subsequent layers of the multilayer which are very much more weakly bound reach equilibrium with the surrounding atmosphere with very low degrees of coverage. The tightly bound moisture does not desorb under vacuum and so is frequently referred to as irreversible water²⁴. At higher values of relative humidity capillary condensation occurs and the pore-shaped voids in the film begin to fill with liquid water²⁵. Capillary condensation can be considered as a consequence of the meniscus curvature in the filling pore, implying a tighter bonding of molecules than they would have as part of a flat surface. The meniscus is therefore in equilibrium with a vapor pressure depressed below saturation, the depression increasing with meniscus curvature, that is with decreasing pore radius. At any value of relative humidity, therefore, there is a critical pore radius such that larger pores will tend to be empty but smaller pores full. As relative humidity increases larger pores fill. The record of the moisture uptake of the film at constant temperature, known as the adsorption isotherm, is therefore a record of the distribution of pore sizes in the film. Figure 1 shows a typical adsorption isotherm after Ogura²⁵ together with the distribution of pore sizes calculated from it. Desorption isotherms are more difficult to measure than adsorption and they frequently show hysteresis probably due to a nonuniform pore radius. A so-called ink-bottle pore will fill at a higher value of relative humidity because condensation required a high vapor pressure to start at the broad base. The greater meniscus curvature at the narrow top of the pore however, permits the retention of water in the pore until the vapor pressure falls to a lower value.

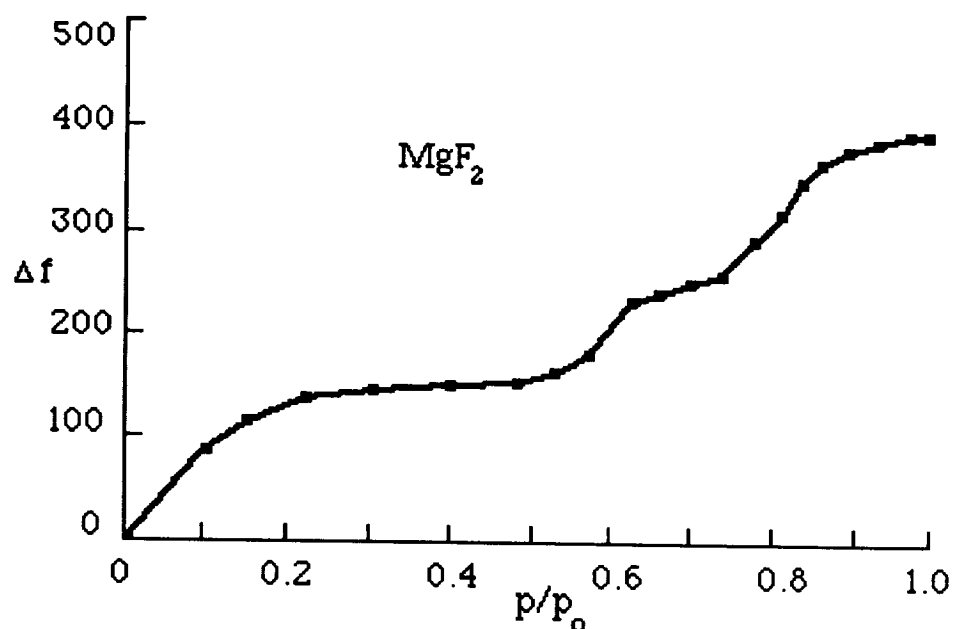


Figure 1a. Adsorption isotherm of a magnesium fluoride layer. Δf is the output of a quartz crystal microbalance that measures the change in mass as the film is exposed to a gradually increasing humidity. The initial mass of this film corresponded to a frequency change of 6307Hz. p/p_0 is the ratio of the partial pressure of water vapor to the saturation partial pressure (after Ogura²⁵).

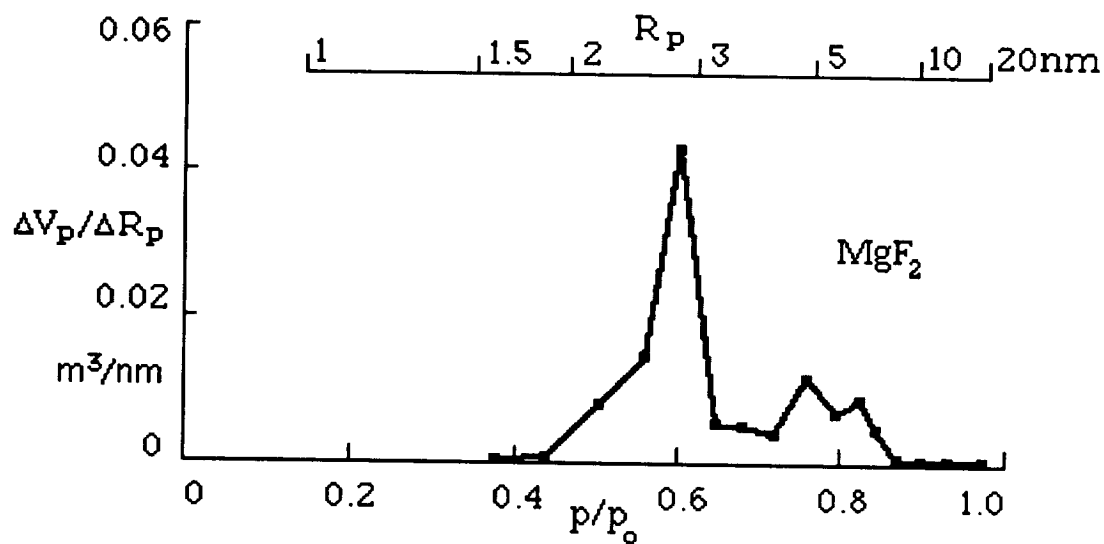


Figure 1b. Pore size distribution of a magnesium fluoride film calculated from the isotherm of figure 1a. All quantities are referred to 1kg of film material. R_p is the pore radius in nm. ΔV_p is the volume of water vapor at stp adsorbed by pores having radii between R_p and $R_p + \Delta R_p$, and is proportional to the geometrical pore volume. (After Ogura²⁵).

4.1.1 Effect on film optical properties

Moisture adsorption affects many film properties. The water replaces a refractive index of 1.0 with one of around 1.33 and so the index of the film rises. For low index films the simple linear interpolation law, expression (3), is usually accurate enough to estimate the changes produced in index and so we can use an adaptation of it to calculate a new value of n_v , the index of the material filling the voids. If f is the fraction of void volume filled with water, then the new value of n_v can be assumed to be;

$$n_v = 1.33f + (1-f) = 1 - 0.33f \quad (5)$$

This new value can then be used together with n_s to estimate the new refractive index. Equation (3) can then be used for low-index films and for high-index films where the packing density is very high, greater than around 0.92. For high-index films with lower packing densities, the Bragg and Pippard expression will usually be better although it will depend on the detailed microstructure. High-index intermediate packing densities, around 0.85 to 0.9, present great difficulties and only qualitative estimates are possible. In all cases however, the index increases and the optical thickness, as a consequence, increases also. Figure 2 shows an adsorption isotherm for magnesium fluoride expressed in terms of refractive index²⁶.

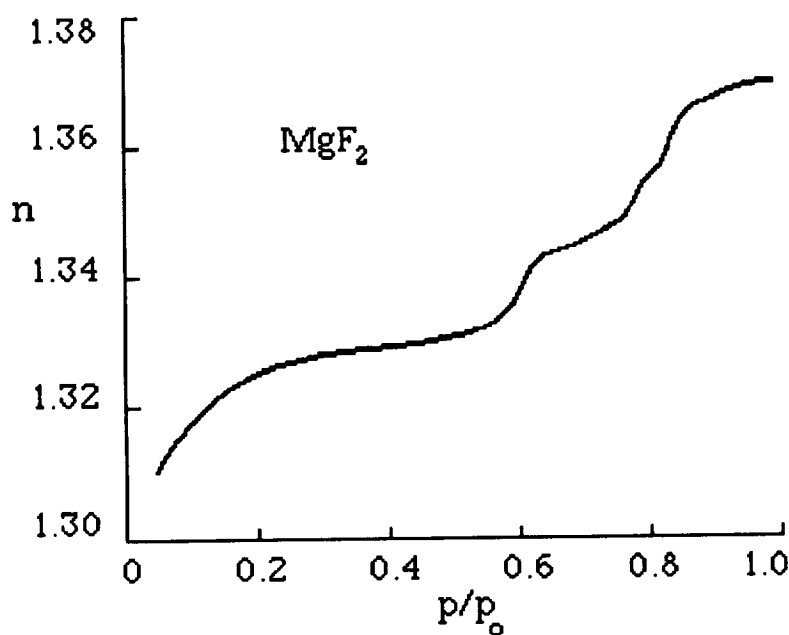


Figure 2. Variation of the index of refraction with humidity of the magnesium fluoride film of figure 1 calculated from the adsorption isotherm on the basis that the columnar index is 1.38. (After Macleod²⁶)

4.1.2 Effect on film mechanical properties

The adsorbed layer of moisture that forms over the entire inner surface of the film blocks the bonds that would otherwise link the columns. An alternative description is that the adsorbed layer of moisture reduces the surface energy of the column surfaces. In the case of the refractory oxides, the reduction in surface energy can be an order of magnitude. As a result, any tensile stress falls. Compressive stress actually rises, probably because of the slight swelling associated with the adsorption of moisture. Because the forces acting between the columns is reduced, the durability of the films falls. Provided that the moisture is present at the very site of a delamination so that it can be involved in a bond transfer rather than a bond rupture followed by attachment of a moisture molecule, then the work of adhesion falls and adhesion failures are made more likely.

4.1.3 Other effects

There are other moisture-induced effects that can be important in particular cases. One example is the moisture and light-induced degradation of zinc sulfide. Under ultraviolet irradiation zinc sulfide loses sulfur and in the presence of either water or oxygen, gains oxygen so that in extreme cases the sulfide can be completely transformed into the oxide²⁷. Atmospheric moisture is also thought to play a part in the sometimes rapid oxidation of films nominally of titanium dioxide but which are oxygen deficient. Such films showing heavy absorption can improve dramatically in transmittance on exposure to the atmosphere after coating. It is not absolutely clear whether or not it is atmospheric oxygen or moisture but the moisture is suspected.

4.2 Multilayers

In multilayers the adsorption process is more complex than in single films because the interfaces between the layers can block the pores. Even an interruption in the deposition of a single material can cause a pseudo-interface²⁸ that causes trapped pores. These obstruction slow down the entry of moisture into the multilayer, which now tends to enter at isolated sites, penetrating deeply into the system and spreading out across individual layers in gradually widening circular patches^{29,30}. The rate of spreading of the patches can vary enormously with the nature of the materials³¹. Equilibrium may be reached almost instantly or it may take months. Multilayers of titania and silica show a remarkably rapid adsorption process while zinc sulfide and cryolite, the materials mostly used for narrowband filters for the visible and near infrared, exhibit very slow adsorption.

4.2.1 Optical effects

It is possible to track the progress of the moisture in a multilayer that has a sharp spectral feature. The increasing optical thickness changes the characteristic and a monochromatic viewing beam can be arranged near the sharp feature so that the moisture-induced shift causes a change from transmitting to rejecting or vice versa. Narrowband filters of the single-cavity type are particularly useful for this observation because the moisture induced changes are simple shifts to longer wavelengths with little or no distortion of passband shape. A diagram, figure 3, shows a typical viewing arrangement. Figures 4 and 5 show the patches that are seen and correspond to the wet parts of the filters.

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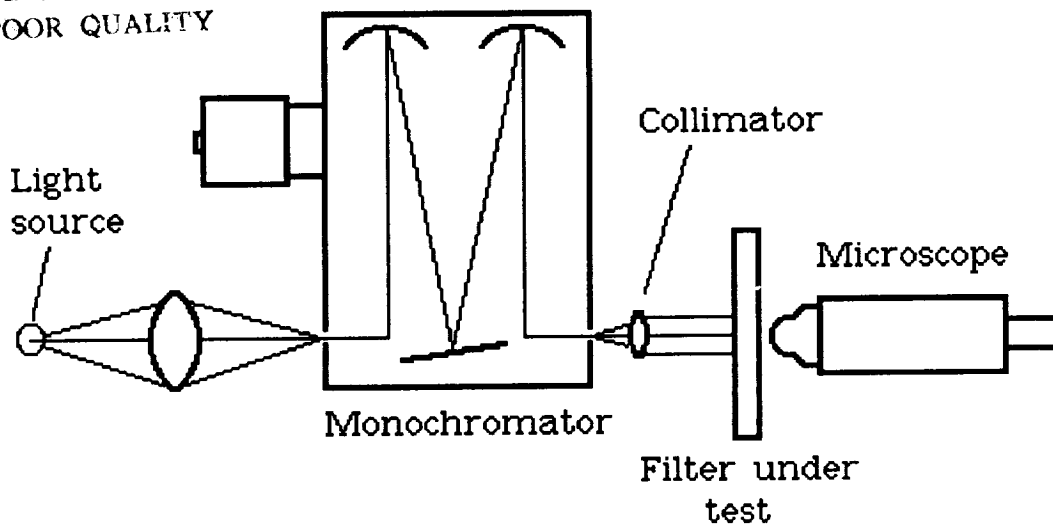


Figure 3. A sketch of the equipment for viewing moisture penetration patterns in optical coatings. (After Macleod and Richmond²⁹)

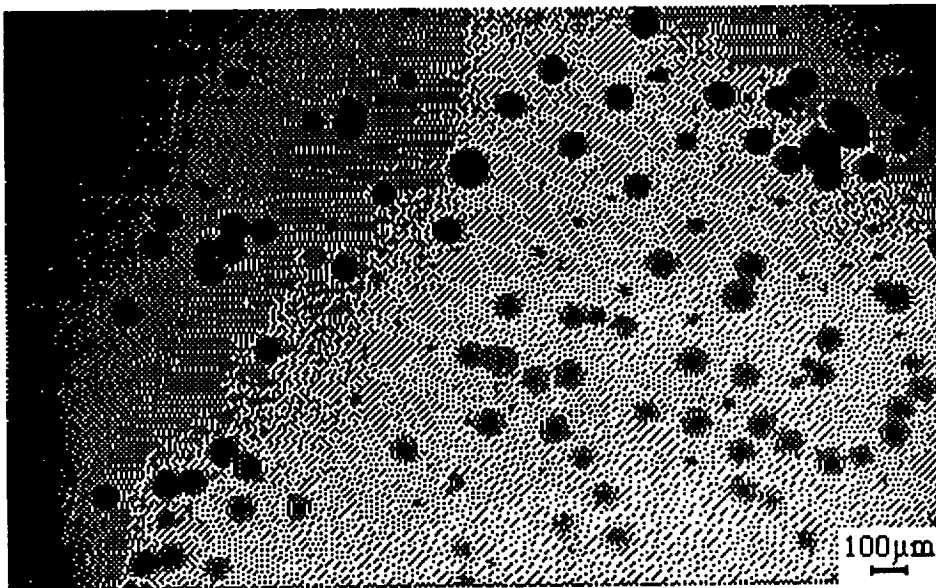


Figure 4a. Water adsorption in a narrowband filter constructed from zinc sulfide and cryolite. The picture was taken at a wavelength of 484nm and a relative humidity of 46%, six days after coating. The patch size at this stage is around 100 μ m. (After Lee³¹)

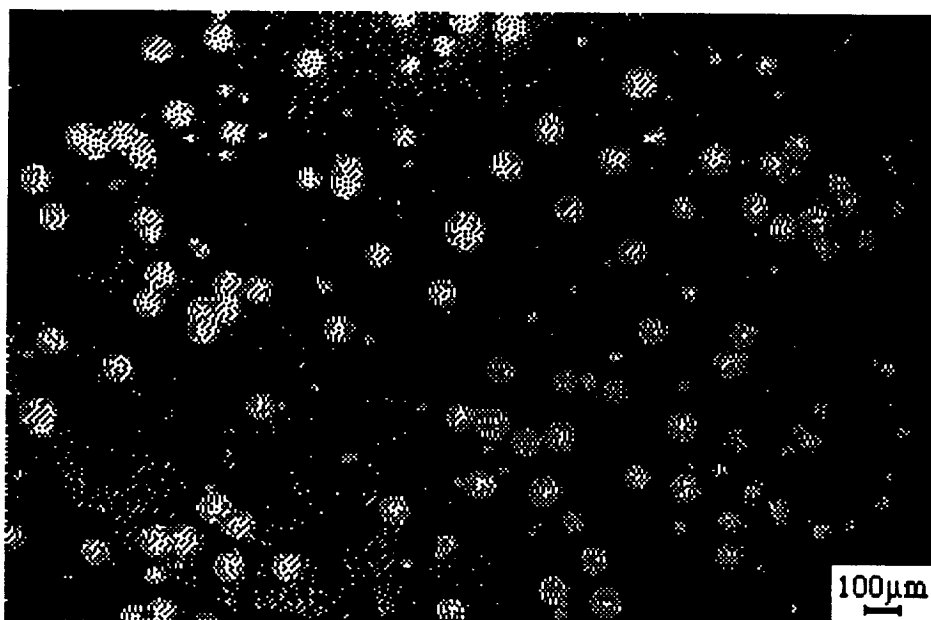


Figure 4b. The same are of the filter of figure 4a but at a wavelength of 507nm. (After Lee³¹)

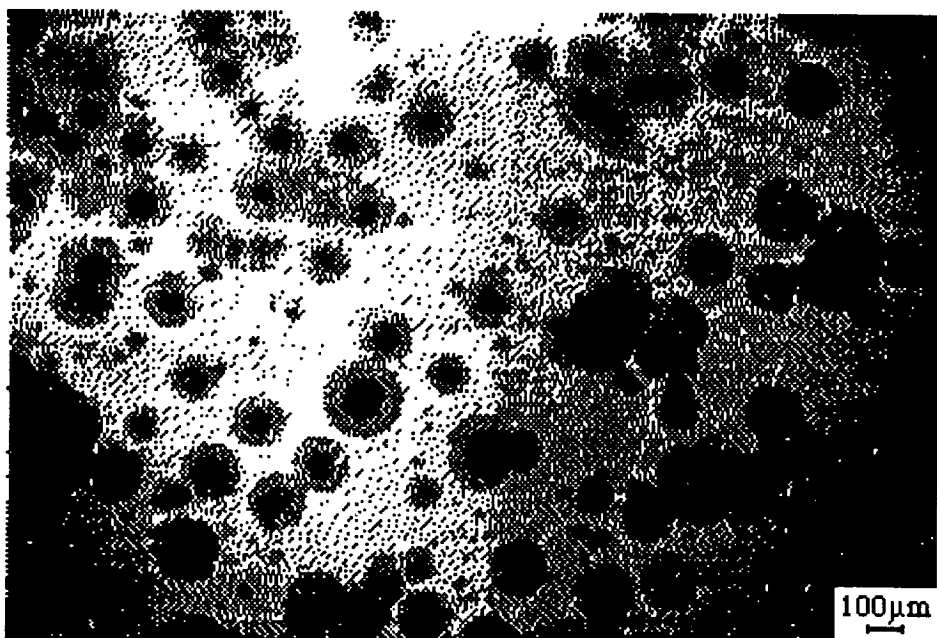


Figure 5a. the filter of figure 4 eight days after coating. The relative humidity has risen to 50%. The wavelength is 485nm and the patches are now around 250μm in diameter. (After Lee³¹)

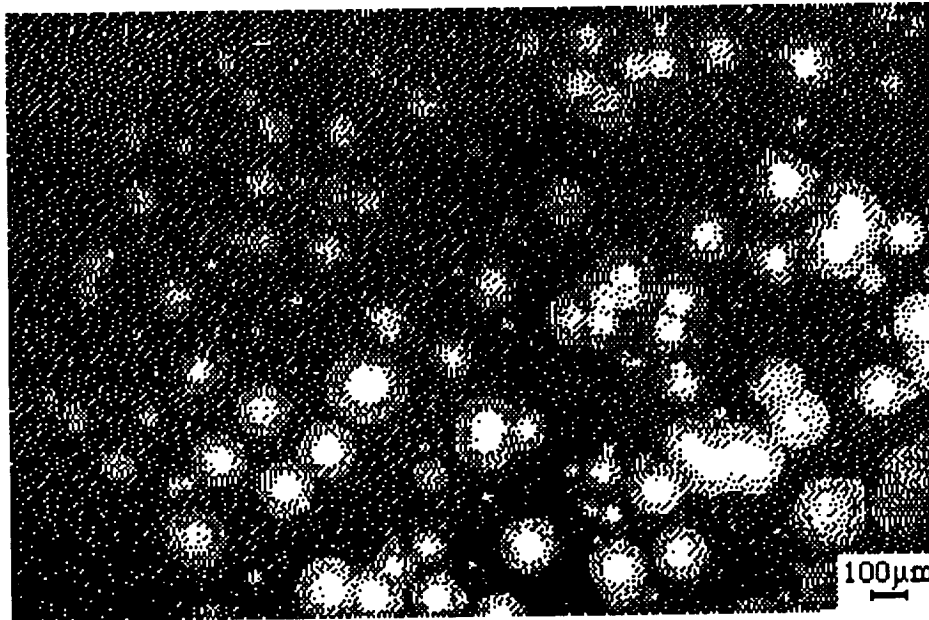


Figure 5b. The filter of figure 5a at a wavelength of 508nm. (After Lee³¹)

The total movement of the filter passband depends on the relative humidity and on the characteristics, especially packing density, of the layers but total drifts in the visible region of several tens of nanometres are not uncommon. Schildt, Steudel and Walther² suggest a relationship for zinc sulfide and magnesium fluoride filters:

$$\Delta\lambda = q \log_{10} P$$

where q is a constant varying from around 1.4 for filters which had aged to around 8.3 for freshly prepared filters. P is the partial pressure of water vapor measured in torr (P should be replaced by $0.76P$ if P is measured in mb) and $\Delta\lambda$ is measured in nm and is arbitrarily chosen as zero for 1 torr (1.3mb). This relationship was found to hold good for the pressure range 1 to approximately 20 torr (1.3 to 26mb).

These patches, then are the origin of the mottled or flecked appearance sometimes remarked in freshly deposited multilayers and often readily visible in fluorescent light, less so in either tungsten illumination or daylight. They are the origin of the unstable behavior of narrowband filter characteristics first observed by Koch¹. The measured optical characteristic of the coating will depend on the area of measurement which may include a range of patches from wet to dry. The filter characteristics in figure 6 are of this type. They can be explained by the performance integrated over the finite area of measurement in the spectrometer.

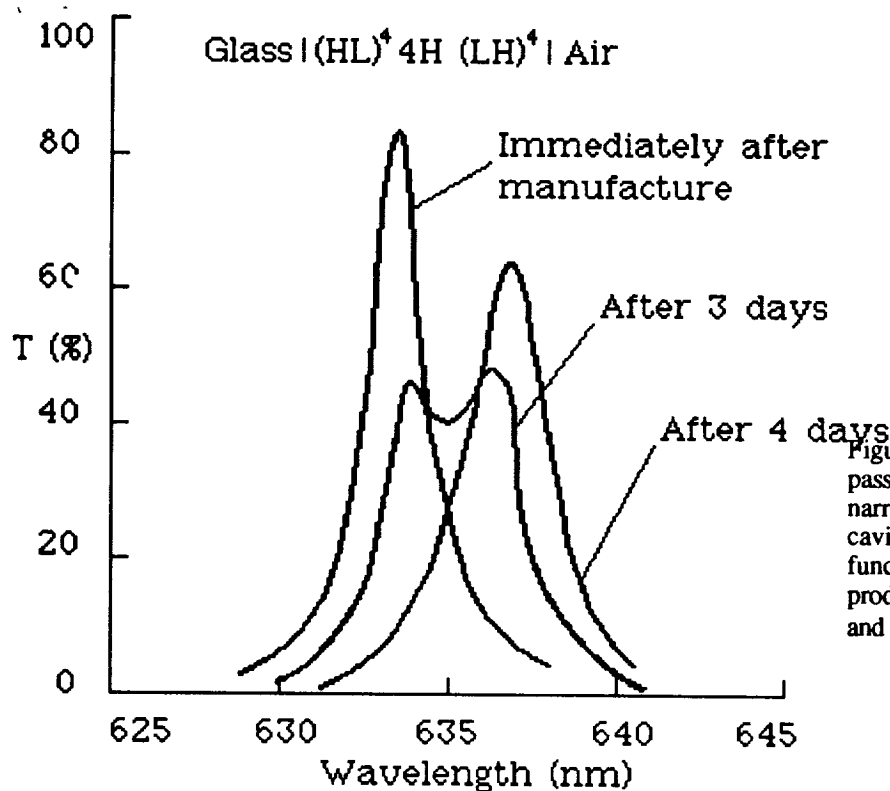


Figure 6. Behavior of the passband of an unprotected narrowband filter of single cavity construction as a function of time after production. (After Macleod and Richmond²⁹)

This behavior of narrowband filters has been studied in detail by Richmond³⁰ and Lee³¹. Reports have also been published by a number of other workers including Gibson and Lissberger³². Richmond points out that there is a significant difference in the behavior of multiple-cavity filters compared with those of single-cavity construction. A single-cavity filter simply moves increasingly towards longer wavelengths with virtually no change in bandwidth or peak transmittance as moisture penetrates to increasing depths. A multiple-cavity filter, on the other hand, experiences a detuning of the cavities as moisture reaches the outermost cavity. This detuning distorts the filter passband and reduces, sometimes drastically, the peak transmittance. Only when the moisture finally passes the last cavity does the peak transmittance begin to be restored but the filter characteristic is shifted, sometimes considerably, from the original dry value. In multiple-cavity filters, then, the penetration patches may not simply represent shifted peak wavelength but rather low, near zero, transmittance. These effects are probably at the root of the sometimes large variations in peak transmittance that can be detected over the surface of narrowband filters and are usually too great to be explained by lack of uniformity in the coating process.

It should be noted that narrowband filters for the near ultraviolet, visible and near infrared are usually supplied with a cemented cover slip over the coatings. This affords a degree of protection that slows down considerably the process of adsorption. Further protection is achieved by sealing the edges of the cemented assembly. If the cementing is not carried out immediately the coating chamber is vented then the patches may appear and will be preserved in the cementing process. They can be detected by examination in monochromatic light as described above. It is difficult to assess the likely life of a filter once it has been covered in this way. Some filters last for many years with no apparent change while others appear to drift at even an early age. Often eventual failure is a

delamination that usually starts at the edge of the filter and gradually spreads inwards. Submission to high temperatures should be avoided. Intense ultraviolet irradiation can also affect the zinc sulfide that is the usual high-index material and should be avoided if possible.

4.2.2 Nature of penetration sites

The nature of the sites where the moisture penetration occurs is not completely understood. Clearly their incidence is such that they cannot be explained as normal microstructural features but rather as exceptional defects of structure. Lee³¹ carried out a series of experiments using zinc sulfide and cryolite filters, the usual narrowband filter materials, in order to discover what might be responsible for them. He found that virtually any departure from perfection in the substrate or process increased considerably the incidence of patches. Dust particles, scratches, substrate roughness and contamination due to omission of the glow discharge cleaning step, all caused great increases in the number of patches. On the other hand the use of superpolished substrates reduced the incidence of patches by a factor of four. Studies of the rate of moisture penetration led Lee³¹ to suggest that the point of moisture entry should be similar to a very long and thin fissure. Such a fissure is often present around a nodular defect and although the evidence is not completely conclusive, nevertheless it all points strongly towards nodules as the culprits.

4.2.3 Mechanical effects

The penetration defects may also act as stress concentrators initiating adhesion failures, which are further encouraged since the presence of moisture reduces the work of adhesion. It is not surprising, therefore, that the penetration sites should often become the centers of blisters when the stress in the outer layers is compressive, as is especially the case with zinc sulfide.

4.2.4 Thermal effects

When the temperature of a multilayer is raised, the adsorbed moisture tends to desorb. In most multilayers the temperature coefficient of optical thickness is such that the shift on increasing temperature should be towards longer wavelengths. Desorption effects can slow or even reverse this tendency. Pelletier and his colleagues³³ have found quite bizarre changes in narrowband filters of the single-cavity type constructed from zinc sulfide and cryolite. The changes depend on the environmental history but are virtually unpredictable. Again those filters that have been protected with cemented covers do not show changes to quite the same degree. Cements, however, tend not to withstand too well subjection to very high temperatures and so care should be taken not to exceed the temperature specification of the manufacturers otherwise delamination of the assembly will be encouraged.

Baking is frequently suggested as a way of stabilizing narrowband filters and certainly seems to have effects that can be beneficial. The changes that take place in the layers are not well understood but certainly desorption of much of the moisture that is present in the coatings occurs as a first step. It is unlikely that baking to several hundred degrees Celsius could increase the solidity of the films so as to reduce their moisture sensitivity. The most likely process is a slight tendency for the smaller voids in the film to coalesce into larger ones leaving the total void volume unchanged. Such a process is predicted by the molecular annealing models of Müller³⁴. These larger voids would require higher relative humidity to fill by capillary condensation and so at lower relative humidity the coating would drift more slowly. At rather higher levels of humidity once liquid water were present in the films, the patches could spread much more rapidly. This might explain

the somewhat conflicting experimental observations that baking can apparently sometimes slow down and sometimes increase the rate of moisture spreading in a coating. In cemented filters, the moisture is trapped in the layers and may be redistributed by the baking process.

5 Stabilization by Ion-Assisted deposition

In order to reduce the effect of moisture on optical coatings, their packing density must be increased. The low packing density associated with thermally evaporated thin films appears to be due to geometrical shadowing of parts of the growing film together with a limited mobility of the condensing molecules that prevents them from migrating into the voids created by the shadowing^{35,36}. To eliminate the voids, additional energy must be supplied to the growing film. This is the idea behind the processes that can be classified as ion assisted in which the growing film is subjected to ion bombardment^{37,38}. In the simplest method, the classical ion-assisted process, thermally evaporated films are bombarded with ions of several hundred eV energy derived from a hot cathode Kaufman³⁹ ion source. The benefit of ion-assisted deposition in reducing moisture sensitivity of coatings was demonstrated clearly by Martin et al⁴⁰. Here the materials were zirconium dioxide and silicon oxide and under bombardment with a flux of $16\mu\text{Acm}^{-2}$ of argon ions of 600eV energy the moisture sensitivity of a rather simple narrowband filter was virtually eliminated. Certain types of bias sputtering⁴¹ also include such bombardment as does ion plating, and similar results have been achieved by sputtering by Motovilov⁴² and by Holm and Christensen⁴³. According to theoretical analyses by Müller⁴⁴, the principal effect is one of momentum transfer that causes molecules to move deeper into the film and pack more tightly to eliminate the voids. However all effects are not completely beneficial. There are chemical changes due to differential sputtering of film components that can cause optical absorption. Furthermore, ion-assisted deposition has not been so far extended to the zinc sulfide and cryolite combination normal in narrow-band filters. It is fair to say that the ion-assisted process in some form is the most promising possibility we have at the present time for eventually eliminating the adverse effects that moisture has on filter stability.

6 Conclusion

This has been a somewhat abbreviated account of moisture-induced effects in optical coatings and in particular narrowband filters. Moisture is responsible for much of the lack of uniformity and stability observed in such components even leading to catastrophic failure. Ion-assisted deposition is a promising process for eventual elimination of the porous microstructure of films responsible for their moisture sensitivity.